

Nature and Behaviour of WO₃ Thick Film Resistors Properties When Subjected to Firing Temperature

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Abstract

WO₃-based thick film resistors were prepared by using standard screen printing technique. This paper was aimed at studying the nature and behaviour due to effect of firing temperature on resistors fired in the range 500-700°C in air atmosphere. The material characterization was performed by XRD, SEM, and EDAX for elemental analysis. A mixture of monoclinic, triclinic and hexagonal WO₃ was observed in the range 500-700°C. The UV-visible spectra show WO₃ exhibits a shoulder at 230 nm along with an ill-defined band at 260 nm. The maximum optical band gap energy of 4.85 eV was calculated at room temperature. The D.C. resistance of the films was measured by half bridge method in air atmosphere at different temperatures. The films showed decrease in resistance with increase in temperature indicating semiconductor behaviour. The TCR, activation energy and sheet resistivity of films were evaluated at different firing temperatures.

Keywords

WO₃; Thick Films; XRD; SEM; UV; Resistivity; Activation Energy; TCR

Introduction

The electrical properties of thick film system are functions of several factors [Anisur Raheman et.al 1997] such as ingredients, manufacturing technique and sintering history. The main ingredients of thick film include a conducting paste, such as an oxide powder; dielectric phase such as glass frit; and an insulating substrate, such as alumina. The oxides used in thick films can be broadly classified into two groups: metallic where the resistivity usually obeys a power law dependence on temperature, $\rho \propto T^n$, where $n \geq 0$ and semiconducting, where the resistivity usually follows an exponential law, $\rho \propto e^{(E/KT)}$. Several deposition methods have been used to grow undoped and doped WO₃ films such as Spray Pyrolysis, Evaporation, Chemical Vapour deposition, Magnetron Sputtering, Pulsed Laser deposition, a Sol Gel

technique and a Screen Printing technique [Joseph Benny et.al 1999]. The screen printing technique was introduced in the later part of the 1950's to produce compact, robust and relatively inexpensive hybrid circuits for many purposes and it is a viable and economical method to produce thick films of various materials [Ansari et.al 1996, Patil et.al 1998]. Today our environment has been polluted by numerous of gases exhausts from auto and chemical industry. In order to detect, measure and control the gases, one should know the amount and type of gases present in the ambient. Therefore the need to monitor and control these gases has led to the research and development of very large variety of sensors using different materials and technologies. Sensors play an important role in the areas of emissions control, environment protection, public safety, and human health [Kolmakov et.al 2004, Park et.al 2009]. Much more public concern today than ever before over serious environmental issues further promotes the development of sensors with both high sensitivity and rapid response. Metal oxide semiconductor materials such as SnO₂, ZnO, TiO₂, WO₃, Fe₂O₃, ZrO₂, CeO₂, In₂O₃, Cr₂O₃, BaTiO₃, Ga₂O₃ etc. have been well reported as gas sensors in the form of thick film [Guidi et.al 2002]. The use of sensors is basically for industrial process controls, in human health, and for the prevention of hazardous gas leaks, measurements of physical quantities and for controlling some systems, which comes from the manufacturing processes [More et.al 2004]. There are many types of gas sensors that have been used to detect various gases: catalytic gas sensors, infrared gas sensors, semiconductor gas sensors etc.

Tungsten, the third element in group VI B of the Periodic Table, possesses different oxidation states ranging from (0) to (+VI) in various inorganic compounds. WO₃ has the oxidation state (+VI), whose density is higher than Cr and Mo which is found in its

group [Ouis et.al 2013]. Tungsten oxide possesses a polycrystalline structure with a wide band gap semiconductor. Its band gap energy has been mainly by optical absorption varying from about 2.6-3.0 eV. The most common structure of WO_3 is monoclinic with space group $\text{P}2_1/\text{n}$. WO_3 films are reported to have promising electrical and optical properties for various applications like efficient photolysis, electrochromic devices, selective catalysts and gas sensors [Grenqvist 1995, Sun et.al 1996]. Amorphous and polycrystalline WO_3 films are particularly attractive as gas sensors because they show a catalytic behavior both in oxidation and reduction reaction [Kung 1989]. Electrochromic devices which exploit WO_3 are typically in an amorphous form, whereas electrical devices such as gas sensors are in a crystalline form [Takase et.al 1991]. Tungsten also forms other oxides such as WO , W_2O_3 and W_4O_{11} , however in gas sensing the stable WO_3 form is used. Tungsten Oxide is known to be a very promising candidate showing good selectivity for sensing of the air pollutants NO/NO_2 , CO/CO_2 and ethanol [Ahmed et.al 2002, Sberveglieri et.al 1995]. The sensing behaviour of bulk WO_3 is known to be a function of its chemical and physical properties such as Surface area, phase composition, crystallinity, and stoichiometry. Generally, the majority of the WO_3 sensing properties are connected with: (1) the WO_3 structural model is perovskite-type ABO_3 lattice with A site, which remains unoccupied site: (2) The WO_3 is considered as oxygen-deficient or non-stoichiometrical oxides. Additionally, it is accepted that the sensitivity is mainly influenced by the sensing material. The advantages of the resistors fabricated through WO_3 are simple design, long term stability, small size, light weight, low cost, good mechanical strength, high reliability, fast response. However, WO_3 gas sensors have good sensitivity at high temperature between 200 and 500°C [Sun et.al 1996, Solis et.al 2001]. The aim of present work is to prepare WO_3 thick films by standard screen printing technique on alumina substrate and to investigate their Nature and Behaviour of WO_3 thick film resistors properties when subjected to firing temperature.

Experimental

Powder, Paste and Thick Film Preparation

Commercially available white color WO_3 powder (Loba Chem.) is mixed thoroughly in an acetone medium by using a mortar and pestle with a permanent binder (lead borosilicate glass frit with a composition of 70 wt% PbO , 18 wt% SiO_2 , 3 wt% Al_2O_3 , 3 wt% B_2O_3 and 6% TiO_2) [Maissel et.al 1974]. Initially

the fine powder is calcined at 450°C for 2 hours in muffle furnace. The pastes used in screen- printing were prepared by maintaining inorganic to organic materials ratio at 70:30. The inorganic part consisted of a functional material (WO_3) and glass frit. The organic part consisted of 8% ethyl cellulose (EC) and 92% butyl carbitol acetate (BCA). The mixture of WO_3 powder, glass frit and EC was mixed by BCA drop wise until a proper thixotropic properties of paste was achieved. The paste was screen printed onto an alumina substrate (96% pure Kyocera). The details of the technique have been described elsewhere [Garje et.al 2006]. The films were dried under IR lamp for 1 hour in an air to remove the organic binder and fired at 500-700°C for 30 minutes in the muffle furnace for better adhesion. During the firing process glass frit melts and the functional materials are sintered. The function of glass frit is to bind grains together.

Thickness Measurements

The thickness of the WO_3 thick films were measured by using Taylor-Hobson (Taly-step UK) system. The thickness of the films was observed in the range of 15-19 μm .

Material Characterizations

The WO_3 -based thick film material is characterized by X-ray diffraction technique [Miniflex model, Rigaku-Japan, DMAX-2500, $\text{CuK}\alpha$ ($\lambda=1.542\text{Å}$) radiation] for structural analysis, degree of crystallinity and grain size determination for Bragg's angle (2θ) from 20 to 80 degree. The average grain size was determined by using Debye Scherer formula [Cullity 1956].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where D is the grain size, λ is the wavelength of the X-ray radiation (1.542 Å), θ is the angle of diffraction and β is the full angular width of diffraction peak at the half maximum peak intensity. Surface Morphology of the WO_3 thick films was studied by using SEM, (JOEL JED-2300, Japan) with Energy Dispersive Analysis of X-rays, EDAX for chemical composition. The UV-visible optical absorption spectra were measured in the range 200–800 nm. A record spectrophotometer (JASCO UV-VIS-NIR Model No.V-670) was used for these optical measurements.

Electrical Characterization

The DC resistance of the thick film samples was measured by half bridge method as a function of temperature in atmosphere [Sarladevi 1995]. Sheet

resistivity (ρ_s) was determined for each of the samples. Sheet resistivity (ρ_s) = ρ/t , where ρ = resistivity of thick film resistor, t = thickness of the film resistor in micrometers. The effect of temperature on the resistance was studied to determine the TCR and calculated as

$$TCR = \frac{1}{R_0} \left(\frac{\Delta R}{\Delta T} \right) / ^\circ C \quad (2)$$

where ΔR = change in resistance between temperature T_1 and T_2 , ΔT = temperature difference between T_1 and T_2 , R_0 = Initial resistance of the film sample. The activation energy of thick film samples was calculated by the Arrhenius plot using the relation

$$R = R_0 e^{-\Delta E/KT} \quad (3)$$

Where R_0 is constant, ΔE is the activation energy of the electron transport in the conduction band, K is Boltzman constant and T is Absolute temperature.

Result and Discussion

X-ray Diffraction Analysis of WO₃ Thick Film

Figure 1 shows an XRD pattern of WO₃ thick film samples fired at 500-700°C plotted in the range 20-80° (2 θ). The XRD pattern shows several peaks of tungsten oxide phases indicating polycrystalline nature. The observed peaks of WO₃ match well with reported ASTM data confirming polycrystalline structure. The sharp peaks reflexes seen on the pattern indicate that a transformation to a highly ordered crystallite has

occurred in the material. The higher peak intensities of an XRD pattern is due to the better crystallinity and bigger grain size can be attributed to the agglomeration of particles. It is observed that as the firing temperature increases, the major contribution towards monoclinic phase also increases as shown in table 1.

The increase in monoclinic phase (or decrease the Triclinic and Hexagonal phase) with an increase in the firing temperature may be attributed to an increase the particle size with the firing temperature. The grain size increases with an increase in firing temperature, which is in good agreement with the previous reported work [Ansari et.al 1997].

Figure 1 shows that the diffraction peaks at 2 θ values of 23.7°, 24.2°, 24.9°, 29.4°, 42°, 47.8°, 50.9°, 51.3°, 55.3°, and 56.4° which reveal the formation of the Monoclinic phase [ASTM Card No.43-1035], peaks at 33.9° and 34.7° reveals the formation of Triclinic phase [ASTM Card No.32-1395], peaks 28.0°, 42.4°, 50.5°, 62.8°, and 77.6° reveals the formation of Hexagonal phase [ASTM Card No.33-1387]. Peak 33.8° reveals the formation of Cubic phase [ASTM Card No.46-1096]. Some peaks of Al₂O₃ are due to the alumina substrate. The average grain sizes for the film samples calculated by using Scherer formula [Culity 1956] are found to be 46.42, 51.09, 54.98 nm (± 2 nm) at 500, 600 °C and 700 °C (± 2 °C) respectively, which are in good agreement with the earlier reported values (~ 55 nm)[Blo et.al 2004].

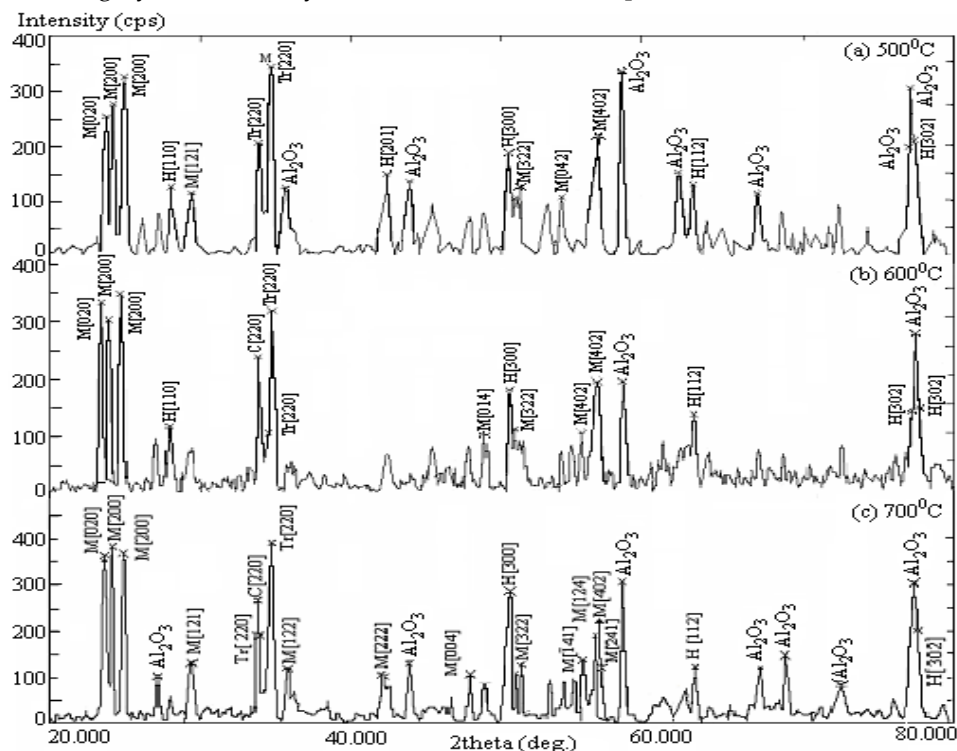


FIG. 1. XRD PATTERN OF WO₃ THICK FILMS FIRED AT 500, 600, 700°C

TABLE 1. THE PRESENCE OF % RELATIVE PHASES OF WO₃ THICK FILM FIRED AT DIFFERENT TEMPERATURE

Firing Temp (°C)	M-WO ₃	Tr-WO ₃	C-WO ₃	H-WO ₃	Al ₂ O ₃
500	37.51	12.75	-----	18.52	31.24
600	49.96	12.73	7.24	16.06	14.00
700	50.79	10.70	5.24	11.67	21.60

Micro Structural Analysis by SEM

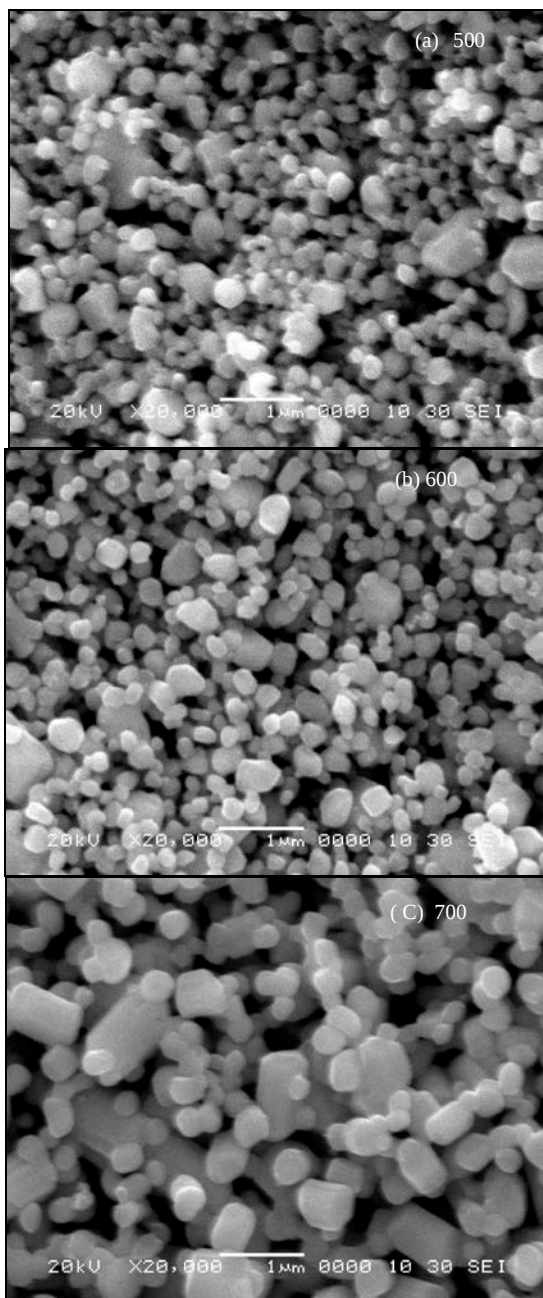
FIG. 2. SCANNING ELECTRON MICROGRAPH OF WO₃ THICK FILMS FIRED AT 500,600,700°C.

Figure 2 shows the SEM micrographs of WO₃ thick films for studying the surface morphology. The SEM micrographs of WO₃ thick films fired at 500-700°C shows polycrystalline structure with number of pores (voids) distributed on the surface of the film, basically

due to evaporation of organic binder during the firing of the films. The particle size being 325, 394, 504 nm (± 2 nm) at 500°C, 600°C and 700°C (± 2 °C) respectively was observed for the WO₃ thick films. The average particle size observed in SEM is much higher than that estimated from bulk XRD data, indicating agglomeration of the particles.

Elemental Analysis

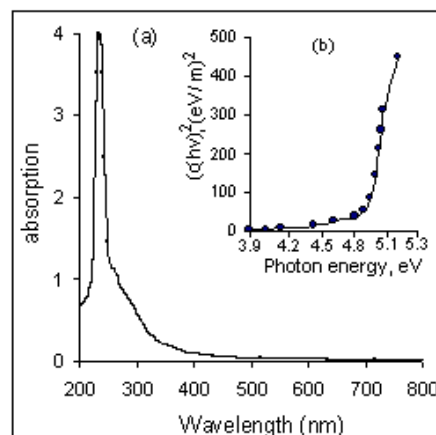
The EDAX analysis of WO₃ thick films showed presence of only W and O as expected, no other impurity elements were present in the WO₃ film samples. Also from the EDAX spectra, it is found that wt% and at% of W and O are nearly matched as illustrated in Table 2.

TABLE 2. COMPOSITION OF THE WO₃ THICK FILMS FIRED AT 500, 600, 700°C.

Sample (WO ₃)			Firing temperature ,°C			
	500		600		700	
Wt %	W	O	W	O	W	O
Mass %	91.56	8.44	90.67	9.33	90.85	9.15
At %	48.56	51.44	45.83	54.17	46.37	53.63
Error %	0.42	0.41	0.99	0.96	0.41	0.39

Optical Studies

Figure 3 (a) shows the optical absorbance spectra of WO₃ powder sintered at 450°C in the wavelength range 200–800 nm. It is seen that the UV spectrum of WO₃ exhibits a shoulder at 230 nm along with an ill-defined band at 260 nm. The variation of optical density with wavelength was analyzed to find out the nature of transition involved and the optical band gap. The wavelength at which ' α ' rises suddenly corresponds to the band gap energy estimated. The absorption coefficient is found to be 4.0 supporting the presence of direct band gap [Desai et.al 1993].

FIG3.(a) ABSORPTION SPECTRA OF WO₃ POWDER SINTERED AT 450°C (B) PLOTS $(\alpha h\nu)^2$ AGAINST PHOTON ENERGY FOR WO₃

The nature of the transition is determined by using the

relation-3 [Kokate et.al 2006]

$$\alpha = A (h\nu - E_g)^{1/2}/h\nu \quad (4)$$

Where E_g is the optical band gap energy, A is a constant. Here n is equal to 1 for direct gap. The plot of $(\alpha E)^2$ as a function of the Photon energy ($h\nu$) of the incident radiation has been shown in Figure 3 (b). It is found that the plot is nonlinear indicating absence of indirect transition. The band edge can be evaluated from the intercept of the extrapolated linear part of the curve to zero absorption with the energy axis. The corresponding value of E_g is found to be 4.85 eV. The maximum optical band gap energy of WO_3 has been reported with $E_g = 3.15$ eV [Washizu et.al 2003]. The difference in present case may be attributed to the different mechanism and technique.

Electrical Characterization

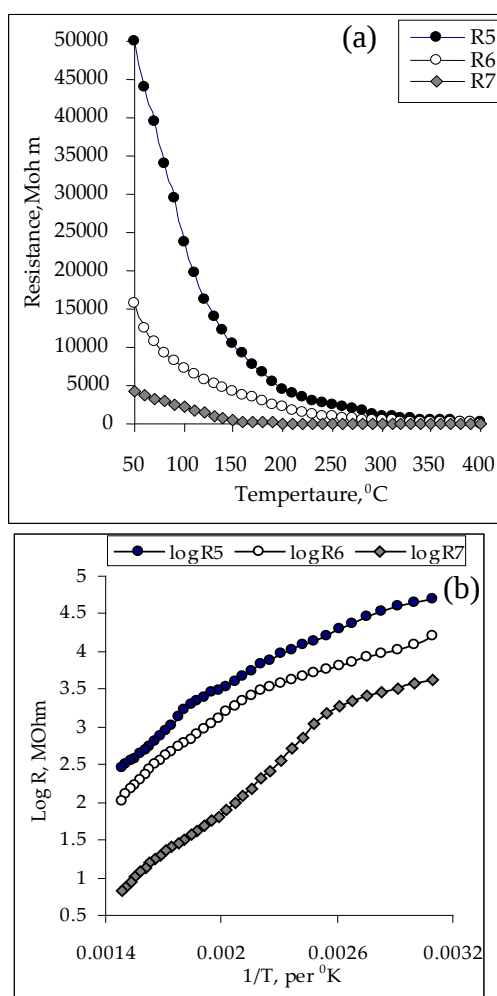


FIG 4. VARIATION OF (a) RESISTANCE WITH TEMPERATURE AND (b) LOG R WITH RECIPROCAL OF TEMPERATURE OF WO_3 THICK FILMS FIRED AT 500, 600, 700°C.

The DC resistance of the WO_3 thick films fired at 500-700°C ($\pm 2^\circ\text{C}$), was measured by using half bridge method as a function temperature. The resistance of

thick films decreases with increase in temperature showing semiconducting behavior. Figure 4(a) shows the resistance variation of WO_3 thick films fired at 500-700°C ($\pm 2^\circ\text{C}$) temperatures in air. Tungsten oxide thick film samples exhibited three regions of resistance similar to SnO_2 thick film Sensors [Chiorino et.al 2001]. The plot shows different conduction region: (i) continuous fall of resistance, (ii) an exponential fall region and (iii) finally saturation region. Any increase in temperature of thick film causes the electrons to acquire enough energy and cross the barrier at grain boundaries [Borse et.al 2008, Windichmann et.al 1979]. There can be decrease in potential barrier at grain boundaries, since at higher temperature the oxygen adsorbates are desorbed from the surface of the films. There is a decrease in resistance with increase in temperature indicating semiconducting behavior, obeying $R=R_0 e^{-\Delta E/KT}$ in the temperature range of 50 to 400°C. For WO_3 film samples fired at 500-700°C, initially resistance is falls linearly up to a certain transition temperature. After the transition temperature, the resistance decreases with exponential fashion and finally saturate to steady level. The transition temperature depends on firing temperature of the film. The initially value of WO_3 thick film resistance in air atmosphere (at 50°C) was 49990, 15780, 4270 Mohm fired at 500, 600, 700°C respectively. Figure 4 (b) shows log R versus reciprocal of temperature ($1/T$) variation of WO_3 thick films fired at 500-700°C.

This variation is reversible in both heating and cooling cycles obeying the Arrhenius equation $R=R_0 e^{-\Delta E/KT}$. It is seen that the curve has two distinct regions of temperature namely low temperature region (323 to 393°K at 500°C, 323 to 393°K at 600°C, 323 to 383°K at 700°C) and high temperature region (543 to 633°K at 500°C, 553 to 663°K at 600°C, 563 to 673°K at 700°C). The activation energy in the lower temperature region is always less than the energy in the higher temperature region because material passes from one conduction mechanism to another. The earlier reported value of activation energy is 0.82 eV [Mohammad et.al 2009]. In low temperature region, the increase in conductivity is due to the mobility of charge carriers which is dependent on the defect/dislocation concentration. So, the conduction mechanism is usually called the region of low temperature conduction. In this region, activation energy decreases, because a small thermal energy is quite sufficient for the activation of the charge carriers to take part in conduction process. In other words, the vacancies/defects weakly attached in lattice can easily

migrate (extrinsic migration). Hence increase in the conductivity in the lower temperature region can be attributed to the increase in charge mobility. In high temperature region, the activation energy is higher than that of low temperature region. In this region the electrical conductivity is mainly determined by the intrinsic defects and hence being called high temperature or intrinsic conduction. The high values of activation energy obtained for this region may be attributed to the fact that the energy needed to form defects much larger than the energy required for its drift. For this reason, the intrinsic defects caused by the thermal fluctuations determine the electrical conductance of the film samples only at elevated temperature. It is observed that TCR increases, sheet resistivity decreases with an increase in firing temperature, which may be attributed to an increase the grain size with the firing temperature. The variation of grain size, Sheet resistivity, TCR and activation energy of the WO₃ thick films fired at temperatures of 500-700°C is summarized in Table 3.

TABLE 3. GRAIN SIZE, TCR, SHEET RESISTIVITY AND ACTIVATION ENERGY OF WO₃ THICK FILMS FIRED AT 500,600, 700°C [THICKNESS OF =16MM]

Firing Temp (°C)	Grain Size (nm)	TCR, x 10 ⁻³ (°C)	Q _s x10 ¹⁰ Ω/□	A.E, eV	
				Low T.R	High T.R
500	46.52	1.227	0.764	0.1760	0.5124
600	51.09	3.449	0.620	0.1570	0.4852
700	54.98	6.168	0.416	0.1521	0.2597

Conclusion

WO₃-based thick films deposited on alumina substrate using screen printing technique showed semiconductor behaviour. XRD analysis shows the structure of WO₃ films is polycrystalline in nature. The average grain size of WO₃ thick films increases with an increase in firing temperature. TCR increases, sheet resistivity decreases with an increase in firing temperature. It also shows voids between the particles basically due to evaporation of the organic solvent during the firing of the films. From optical studies, the direct band gap energy value was found to be 4.85 eV. The UV-visible spectrum of WO₃ exhibits a shoulder at 230 nm along with an ill-defined band at 260 nm.

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